# ELECTRONIC STRUCTURE OF ZINC-BLENDE $Zn_{0.5}Co_{0.5}Se$: THEORETICAL STUDY*

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In this paper we present partial densities of states for spin-polarized antiferromagnetic phase of $Zn_{0.5}Co_{0.5}Se$ as well as schematic layouts of the bands, obtained using the *ab initio* self-consistent semi-relativistic linear muffin tin orbital method. We also present, from theoretical point of view, the analysis of influence of the transition metal cobalt on the electronic structure of a pure ZnSe.

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## 1. Introduction

Investigations of electronic structure of ZnSe using *ab initio* self-consistent semi-relativistic linear muffin tin orbital (LMTO) method has shown that, in this semiconducting compound with direct energy gap ($\Gamma_8^v - \Gamma_6^c$), the lowest band of the occupied valence states is mainly $s$-like and is localized on Se-anion. Next, the valence band maximum has Se $4p$ character and the Zn $3d$ bands fall in the middle of the $sp$ valence band manifold [1]. The introduction of a small amount of cobalt, which has nonzero magnetic moment, transforms ZnSe into a diluted magnetic semiconductor (DMS). The $d$ states of a transition metal are split into two groups of sublevels with spin-up and spin-down by the exchange interaction (Slater splitting). The proper description of band structure of DMS requires inclusion of spin effects of transition metal $3d$ shell.

## 2. Method of calculation

The electronic structure of $Zn_{0.5}Co_{0.5}Se$ has been determined using the *ab initio* self-consistent semi-relativistic LMTO method [2,3]. The so-called "combined correction term" has been included in the calculations [3]. The exchange--correlation local-spin-density approximation (LSDA) potential has been used in the form proposed by Vosko–Wilk–Nusoir [4]. In the calculations of spin-polarized antiferromagnetic phase the zinc-blende structure of $Zn_{0.5}Co_{0.5}Se$ has been considered and the lattice constant equal to 5.656 Å has been applied. The openness of the crystal structure was dealt in a standard way by placing additional "empty spheres" into the unit cell according to the Freeman procedure [5]. The alloy environment in $Zn_{0.5}Co_{0.5}Se$ has been simulated by an ordered supercell $Zn_2Co_2Se_4$ + 8 empty spheres. Two cobalt atoms with opposite spins were treated as two different types of atoms. The calculations were carried out in a single energy panel, using $4s$, $4p$ and $3d$ basis functions for Zn; $4s$, $4p$ and $4d$ functions for Se, and $4s$, $4p$ and $3d$ for Co. The self-consistency criterion was based on the difference between the input and the output potential which should be smaller than 0.001 Ry. The number of the 79 $k$ points were used in the irreducible part of the Brillouin zone (1/48) during the numerical procedure.

## 3. Numerical results and discussion

The results of calculations in $Zn_{0.5}Co_{0.5}Se$ are presented in Figs. 1 and 2. In Fig. 1 partial densities of states on each site resulting from our calculation are presented. Notice that in Fig. 1 some curves (either $d$ or $s$) are scaled in order to show them on the same scale. Figure 2 illustrates the chosen schematic layouts of the self-consistent bands for $Zn_{0.5}Co_{0.5}Se$ deduced from the potential-parameter-related quantities $B_l$, $C_l$ and $A_l$ which specify the square-well pseudopotential: the bottom, the band center and the top of the $l$ bands, respectively [3]. The zero of the energy scales in both cases (Figs. 1 and 2) is put at the Fermi energy. As it can be seen from Fig. 1, the theoretical alloy $Zn_{0.5}Co_{0.5}Se$ demonstrates metallic properties although ZnSe and hypothetical zinc-blende CoSe compounds belong to group of semiconductors [6]. A similar situation has been observed for $Zn_{0.5}V_{0.5}Se$ [7]. The lowest occupied states in the presented energy range (Fig. 1) are mainly $s$-like and are localized on an anion. These states are not shifted from the Fermi energy, as compared with a pure ZnSe [1]. The Zn-3$d$ bands fall between the lowest Se-$s$ like states and upper broad Se-$p$ and Zn-$s$ like bands, like in the host crystal. The positions of these Zn-$d$ states are changed downward in comparison with the pure ZnSe by the order of 2 eV (measured from the Fermi energy). Summing up, in the region from −15 to −5 eV, the electronic structure of $Zn_{0.5}Co_{0.5}Se$ is very similar and coincides in energy to the pure ZnSe. In the energy region of (−5)–0 eV we do not observe a significant shift of broad Se-$p$ and Zn-$s$ like bands towards lower energy, due to the interaction with transition metal 3$d$ states, like in $Zn_{0.5}V_{0.5}Se$ [7]. The electronic structure for energy higher than 5 eV (counted from the Fermi energy) predominantly consists of Zn-$p$ states and Se-$d$ states with appreciable contribution of Co-$p$ states. This behavior is typical of all transition metals in ZnSe [6,7]. The band structure of $Zn_{0.5}Co_{0.5}Se$ is determined by Co-$d$ electrons in

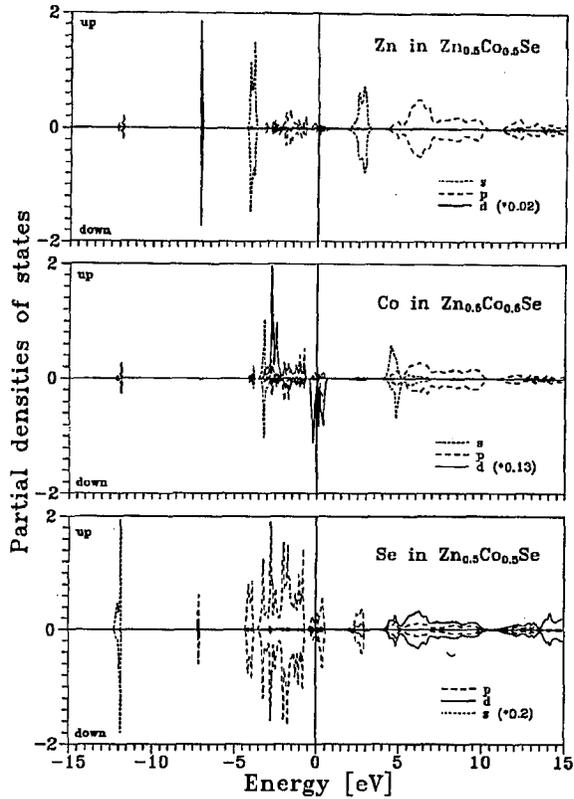Fig. 1. Partial densities of states for Zn, Co and Se sites in $Zn_{0.5}Co_{0.5}Se$. The zero of scales is at the Fermi energy.

the energy region from −4 to 1 eV. From Fig. 1, it is clearly seen that the main part of the Co-$d$ states is localized closely to the Fermi energy (zero in scale) as well as polarized, and plays a main role in the transformation of a ZnSe semiconductor into a metallic compound of $Zn_{0.5}Co_{0.5}Se$. The Co-$d$ states with spin-down are centered at −0.35 eV and they are occupied in the main part, whereas the spin-up Co-$d$ band is completely occupied and is centered at −2.29 eV (Fig. 2). The separation of 1.94 eV between them constitutes the effective $d$ bands exchange splitting and seems to be a reasonable value, while comparing to other transition metals in ZnSe [6]. From Fig. 1 it is also clear that the spin-up Co-$d$ states strongly hybridize with $p$ states of Se-anion, on the contrary to the spin-down Co-$d$ states. For $Zn_{0.5}Co_{0.5}Se$ we do not find negative splitting of anion $p$ states due to $p$–$d$ interaction exchange, like in ferromagnetic $Cd_{0.5}Mn_{0.5}Te$ [8]. In $Zn_{0.5}Co_{0.5}Se$ the energy positions of the Co-$d$ and Se-$p$ bands coincide, but the electrons at the Fermi level are not fully polarized and the splitting of the top of the Se-$p$ like band does not occur. For a fixed $l$-band ($l = s$, $p$ and $d$), a direct comparison between the layouts of ZnSe [1] and $Zn_{0.5}Co_{0.5}Se$ does not show significant changes in energy positions of $B_l$, $C_l$ and $A_l$ for Zn and Se sites. However, one can observe that the layout for
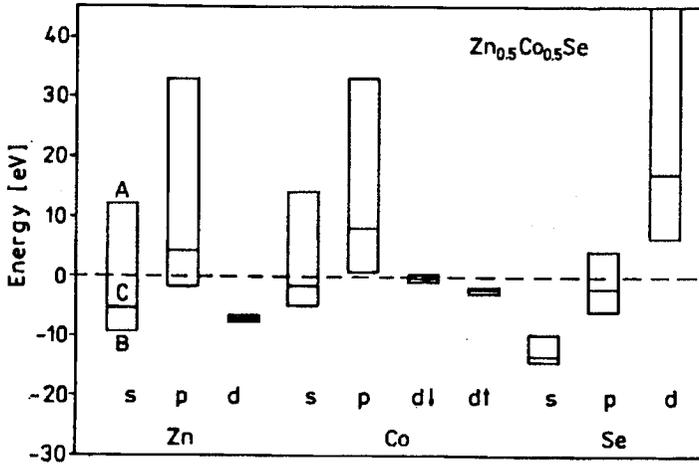
Fig. 2. The schematic of the most important layout of the electronic structure of $Zn_{0.5}Co_{0.5}Se$. The bars depict the extent of the $n$, $l$ bands as defined by parameters $A_l$ (top of the band), $C_l$ (band center) and $B_l$ (bottom of the band). The zero of scale is at the Fermi energy.

Zn and Se $l$ bands in $Zn_{0.5}Co_{0.5}Se$ are narrower in comparison with the pure ZnSe and ternary $Zn_{0.5}V_{0.5}Se$ [1, 7]. Our calculations allowed us to obtain the magnetic moment for cobalt in $Zn_{0.5}Co_{0.5}Se$ which is equal to $2.13\mu_B$ and $p$–$d$ hybridization is found to reduce the local magnetic moment of Co. Moreover, it produces a small local magnetic moment of about $0.02\mu_B$ on the otherwise nonmagnetic Zn and Se sites.

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